REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TECHNICAL REPORT NO. 02	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD-A.......
4. TITLE (and Subtitle) THE EFFECT OF ADDITIVES ON LITHIUM CYCLING IN METHYL ACETATE		5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT 01 Jan 1974 to 31 Jan 1975
		6. PERFORMING ORG. REPORT NUMBER C-404
7. AUTHOR(s) R. David Rauh and S. Barry Brummer		8. CONTRACT OR GRANT NUMBER(s) N00014-74-C-0205
9. PERFORMING ORGANIZATION NAME AND ADDRESS EIC, Incorporated 55 Chapel Street, Newton, Ma. 02158		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 359-571
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE FEBRUARY 1975
		13. NUMBER OF PAGES 22
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Lithium Corrosion, Lithium Electrode, Lithium Plating, Lithium Secondary Batteries, Methyl Acetate, Nitromethane, Passivation of Lithium, Sulfur Dioxide.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Methyl acetate (MA) was examined as a solvent for use in nonaqueous secondary lithium batteries. The efficiency of cycling lithium on nickel in MA/1M $LiClO_4$ containing less than 10 ppm H_2O was less than 10%. Addition of nitromethane (NM), SO_2 or small amounts of H_2O improved the efficiency markedly. Compared to propylene carbonate (PC), MA plus SO_2

DD $_{1\ JAN\ 73}^{FORM}$ 1473   EDITION OF 1 NOV 65 IS OBSOLETE

20. Abstract (Cont.)

or NM afforded more repeated cycles before failure of the working
electrode. Unlike PC, the open circuit corrosion rate of electro-
deposited lithium in MA is decreased in the presence of additives,
e.g., from about 300 $\mu A/cm^2$ to 70 $\mu A/cm^2$ with $>10^4$ ppm nitromethane,
and to 0 $\mu A/cm^2$, under the proper conditions, with 3M SO_2. The
differences in behavior between PC and MA are attributed to the
greater solubility of the MA-lithium reaction products, allowing
greater opportunity for buildup of additive-induced conductive
films on the metallic deposit.

Disclaimers

The views and conclusions contained in this document are
those of the authors and should not be interpreted as
necessarily representing the official policies, either
expressed or implied, of the Advanced Research Projects
Agency, Office of Naval Research or the U.S. Government.

The citation of trade names and names of manufacturers in
this report is not to be construed as official government
endorsement or approval of commercial products or services
referenced herein.

THE EFFECT OF ADDITIVES ON LITHIUM CYCLING
IN METHYL ACETATE

ABSTRACT

Methyl acetate (MA) was examined as a solvent for use in non-aqueous secondary lithium batteries. The efficiency of cycling lithium on nickel in MA/1M $LiClO_4$ containing less than 10 ppm H_2O was less than 10%. Addition of nitromethane (NM), SO_2 or small amounts of H_2O improved the efficiency markedly. Compared to propylene carbonate (PC), MA plus SO_2 or NM afforded more repeated cycles before failure of the working electrode. Unlike PC, the open circuit corrosion rate of electrodeposited lithium in MA is decreased in the presence of additives, e.g., from about 300 $\mu A/cm^2$ to 70 $\mu A/cm^2$ with $>10^4$ ppm nitromethane, and to 0 $\mu A/cm^2$, under the proper conditions, with 3M SO_2. The differences in behavior between PC and MA are attributed to the greater solubility of the MA-lithium reaction products, allowing greater opportunity for buildup of additive-induced conductive films on the metallic deposit.

INTRODUCTION

In a previous paper, a secondary battery system was described featuring a lithium anode, a soluble or partially soluble cathode, and an electrolyte containing another material, the so-called "precursor." This precursor passivates the lithium against attack by the electrolyte species, via film formation, but is to allow charge and discharge of the metal itself (1). The rechargeability of the lithium electrode was studied in propylene carbonate (PC)/1M $LiClO_4$ containing H_2O, SO_2 or nitromethane (NM). The possible passivation of the electrodeposit by these additives was investigated by monitoring the corrosion rate of lithium plated onto a nickel substrate. It was determined that the additives enhanced the cycling efficiency, probably due to the limitation of solvent reduction during electroplating, which leads to the insulation of some of the deposit. On the other hand, a corrosion rate of 25-40 $\mu A/cm^2$ for the high surface area plated lithium was virtually unchanged in the presence of 0.5M SO_2, 0.1M NM or up to 1000 ppm H_2O. Except for the indirect result that H_2O or SO_2 might be expected to increase the corrosion rate, passivation of the deposit through film formation could not be conclusively demonstrated.

Simple aliphatic esters have obvious appeal as nonaqueous electrolytes for lithium batteries. They are not as hygroscopic as propylene carbonate, yet $LiClO_4$ has been reported as soluble up to 4M in methyl acetate, ethyl acetate, methyl formate and n-butyl formate (2).

1

They may be distilled at ambient pressure, as they are thermally stable at their boiling points, unlike the cyclic esters (3). The specific conductivities of 1M $LiClO_4$ in MA, EA, MF and BF are approximately 7×10^{-3}, 3×10^{-3}, 1.8×10^{-2} and 6×10^{-3} ohm^{-1} cm^{-1}, in the same range as the corresponding value for PC (4.76×10^{-3} ohm^{-1} cm^{-1}) (4).

In analogy to the cyclic esters, we might expect some stability of aliphatic esters toward lithium. However, several observations of reactivity between linear esters and bulk lithium have been reported. Meyers (2) noted slow gassing of MA and MF in contact with lithium and the development of a white coating on the metal after several days exposure; BF appeared inert under the same conditions. All three esters showed enhanced reactivity toward lithium with $LiClO_4$ as a solute, although the H_2O content of these solutions were unspecified. Dampier and Krouse (5) measured the gas evolution up to 74°C from $LiAsF_6$/ester solutions in contact with lithium, and found the order of stability to be MF > MA > EA. Maximum gas evolution was achieved after an initial induction period.

It is the purpose of this study to assess the potential of MA, a representative linear ester, as an electrolytic solvent for lithium cycling and passivation by added precursors SO_2, NM and H_2O. The efficiency of electrochemically cycling lithium on an inert nickel substrate has been measured as a function of additive, open circuit standing time, and cycle number in MA/1M $LiClO_4$ solutions.

EXPERIMENTAL

Reagents were as previously described (1), except for the following: Methyl acetate (Baker Grade) was distilled using a Perkin-Elmer 251 spinning band column at atmospheric pressure and a 2:1 reflux ratio. The middle 60% fraction was collected for use at 56-57°C. This material was found by Karl Fischer analysis to contain less than 10 ppm H_2O. Directly following distillation, the solvent was transferred to a dry-atmosphere, argon-filled glove box.

Solutions were prepared 1M in $LiClO_4$, followed by drying with stirring for three, 24 hour periods with freshly activated Linde 5A, 600 mesh molecular sieve. Karl Fischer analysis showed that solutions so dried contained less than 10 ppm H_2O, while untreated solutions contained approximately 1200 ppm.

Attempts at further freeing the dried solutions of reducible impurities or H_2O by stirring with lithium dispersion resulted in initial yellowing of the solution followed by the production of a white precipitate.

Cell Design and Construction. The "open electrolyte" cell previously described was used in most studies. However, some experiments were carried out using a "closed" cell arrangement. Here, the Teflon masked nickel working electrode was separated from the lithium counter electrode with porous paper. The electrodes and separator were sandwiched between two Teflon hemicylinders, the arrangement fitting snugly into a glass vial.

Electrochemical measurements were made as described earlier (1).

RESULTS

1. Cyclic Voltammetry. Cyclic voltammograms of MA, 1M LiClO$_4$ containing 1200 ppm H$_2$O and 10 ppm H$_2$O, as determined by Karl Fischer analysis, are reproduced in Fig. 1. The electrolyte appears relatively stable in the potential range 4.5 to 1.0V vs. Li/Li$^+$, on platinum. The sweep was not continued below 1.0V because alloying between platinum and lithium changes the character of the substrate. Maximum currents for the dry electrolyte were below 200 μA/cm^2, except at the anodic potential limit. The cathodic current between 1.0 and 2.0V is about twice as large in the wet solution, and presumably this difference arises from reduction of H$_2$O. The small oxidation peak at $\sim$2.0V is increased by holding the potential at 1.0V. Likewise, scanning out to 4.5V results in an increase in reducible substances between 1.0 and 2.0V. Below 1.5V, a general increase in cathodic current is observed even in the dry solution. The reported reaction of MA with lithium (2,5) is, then, probably the consequence of this type of reduction of the solution in this potential region and below.

2. Lithium Cycling Efficiency Studies. Solutions of 1M LiClO$_4$ in freshly distilled MA were prepared and dried as described. Such very dry solutions showed cycling efficiencies of < 3% over at least five cycles for 1 coul/cm^2 lithium deposited onto nickel. Lithium was clearly being deposited, but was electrochemically irretrievable. Plating and stripping current densities were varied between 1 and 20 mA/cm^2 with no improvement.

Cycling solutions containing 1200 ppm H$_2$O yielded some improvement. At 10 mA/cm^2 plating and stripping current, the open electrolyte cell yielded an average of 50% efficiency for 1 coul/cm^2. The separator cell gave 17 to 20% under the same conditions. Experiments varying the plating current densities from 1 to 10 mA/cm^2 were also carried out for the same solution in cells of the latter configuration. The cycling efficiency increased markedly with plating current, as in the case of PC-based electrolytes. One drying with activated molecular sieves provided an intermediate water content of approximately 100 ppm, as determined by Karl Fischer analysis. These solutions showed a cycling efficiency of between 0 and 12%, increasing with increasing plating current density. The results are plotted in Fig. 2.
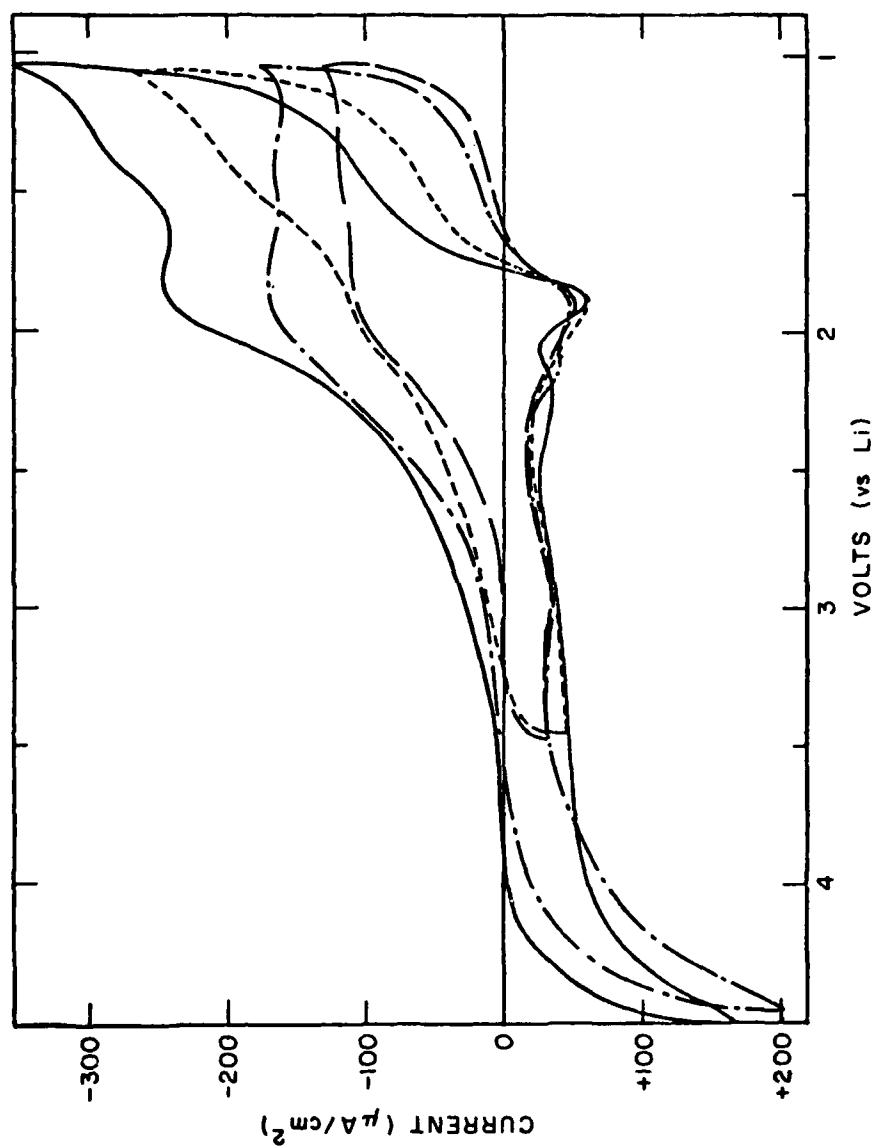
3

Fig. 1: Cyclic voltammograms of 1M LiClO4 in methyl acetate on platinum. Sweep speed = 0.1 V/sec. T = 25°C. (————) 1200 ppm H2O; (———,———) 10 ppm H2O.
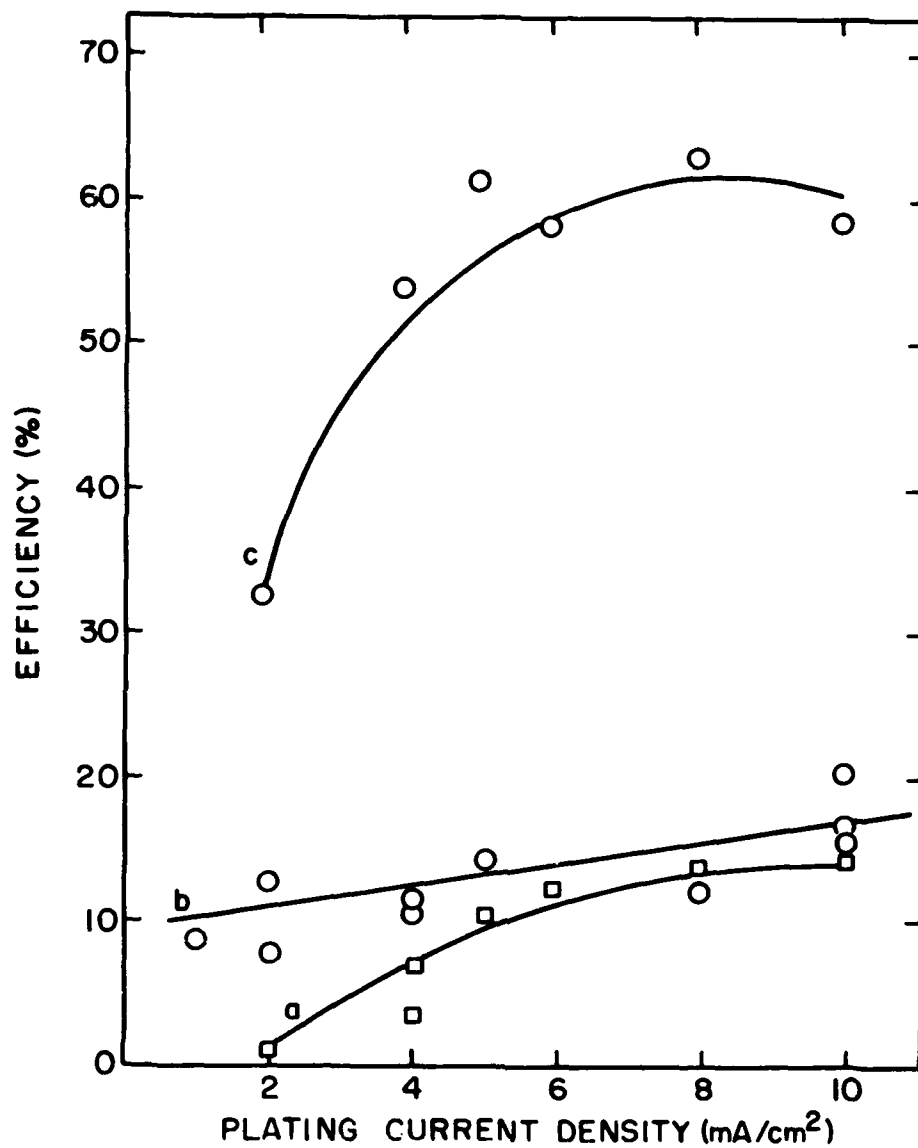
Fig. 2: Efficiency of cycling lithium on a nickel substrate in
methyl acetate, 1M LiClO4, as a function of plating
current. (a) $[H_2O] \simeq 100$ ppm; (b) $[H_2O] \simeq 1200$ ppm;
(c) $[H_2O] \simeq 100$ ppm, $[SO_2] = 3M$.

5

Corrosion currents (i_c) for the wet and partially dry solutions were estimated by plating a known amount of lithium, then monitoring the potential of the working electrode on open circuit stand. When bare nickel became exposed, the potential rapidly became anodic vs. Li/Li^+. The values of i_c varied from 0.15 to 0.35 mA/cm^2, showing considerable scatter for both wet and partially dried solutions (Fig. 3). Within this experimental error, plating current density had no effec: upon i_c.

Corrosion currents were also determined for the "wet" solutions by the method of plating a known amount of lithium, and stripping after various times of open circuit stand. For a plating current of 10 mA/cm^2, the corrosion rate obtained for the "open" cell configuration was 0.3 mA/cm^2 during the first hour of stand, compared to 0.2 mA/cm^2 for the "closed" cell configuration under the same conditions.

3. <u>Effect of Nitromethane (NM)</u>. As is the case with PC, small amounts of NM have a large effect on the cycling efficiency of lithium in MA/1M $LiClO_4$. Fig. 4 shows cyclic voltammograms on a nickel wire electrode in the lithium plating region of MA/1M $LiClO_4$ containing 0, 200, 1000 and 20,000 ppm NM. The increase in the efficiency of stripping lithium is quite evident. In addition, the prewave at 0 to 0.25V vs. Li/Li^+ is absent in solutions containing NM, evidently signalling the suppression of solvent (solution) reduction.

The efficiencies of cycling 1 $coul/cm^2$ of lithium on a nickel substrate in an open electrolyte cell are shown as a function of NM concentration in Fig. 5. Addition of 500 ppm NM is sufficient to raise the efficiency from < 3% to 60% at a plating current of 10 mA/cm^2.

The corrosion of deposited lithium was measured for a plating charge of 1 $coul/cm^2$ at plating and stripping current densities of 10 mA/cm^2. The results are plotted in Fig. 6. It is evident that above $\sim 10^4$ ppm NM, the corrosion rate assumes a more or less constant average value of 70 $\mu A/cm^2$. The plateau of low i_c occurs in the same NM concentration range as the plateau of high efficiency.

Typical chronopotentiograms of plating and stripping lithium in an electrolyte with 2% NM are shown in Fig. 7. If lithium is stripped immediately after plating, the plateau potentials of the two processes are equal but of opposite sign with respect to Li/Li^+ ($\pm 0.245V$, in this case, uncorrected for iR). However, if the deposit is stripped after partially corroding on open circuit, the stripping potential is higher, with a significant anodic overshoot at the beginning of the process. The maximum stripping potential shift on standing is ~ 70 mV at this current density (Fig. 7). This type of behavior indicates the formation of a resistive film on the deposited lithium, which is broken down during the stripping cycle.
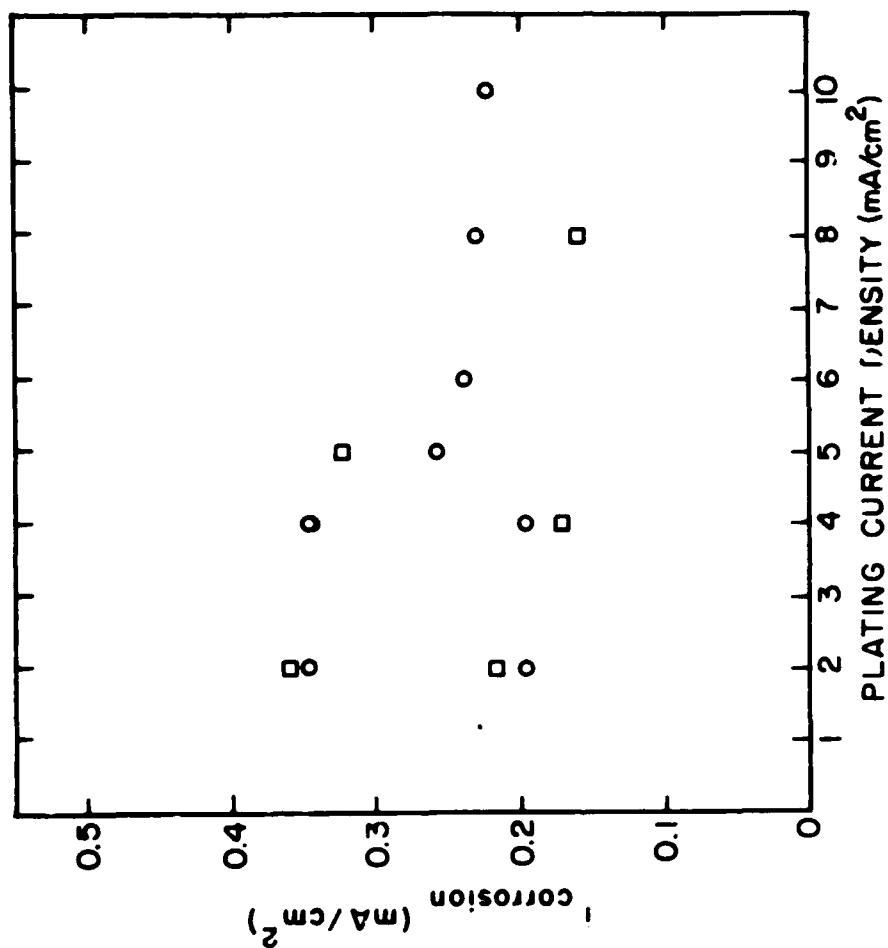
Fig. 3: Open circuit corrosion rate of lithium electrodeposited onto nickel, as a function of plating current density. Amount plated (Q_p) = 1 coul/cm². (O) methyl acetate, 1M $LiClO_4$, ~100 ppm H_2O; (●) methyl acetate, 1M $LiClO_4$, 1200 ppm H_2O.
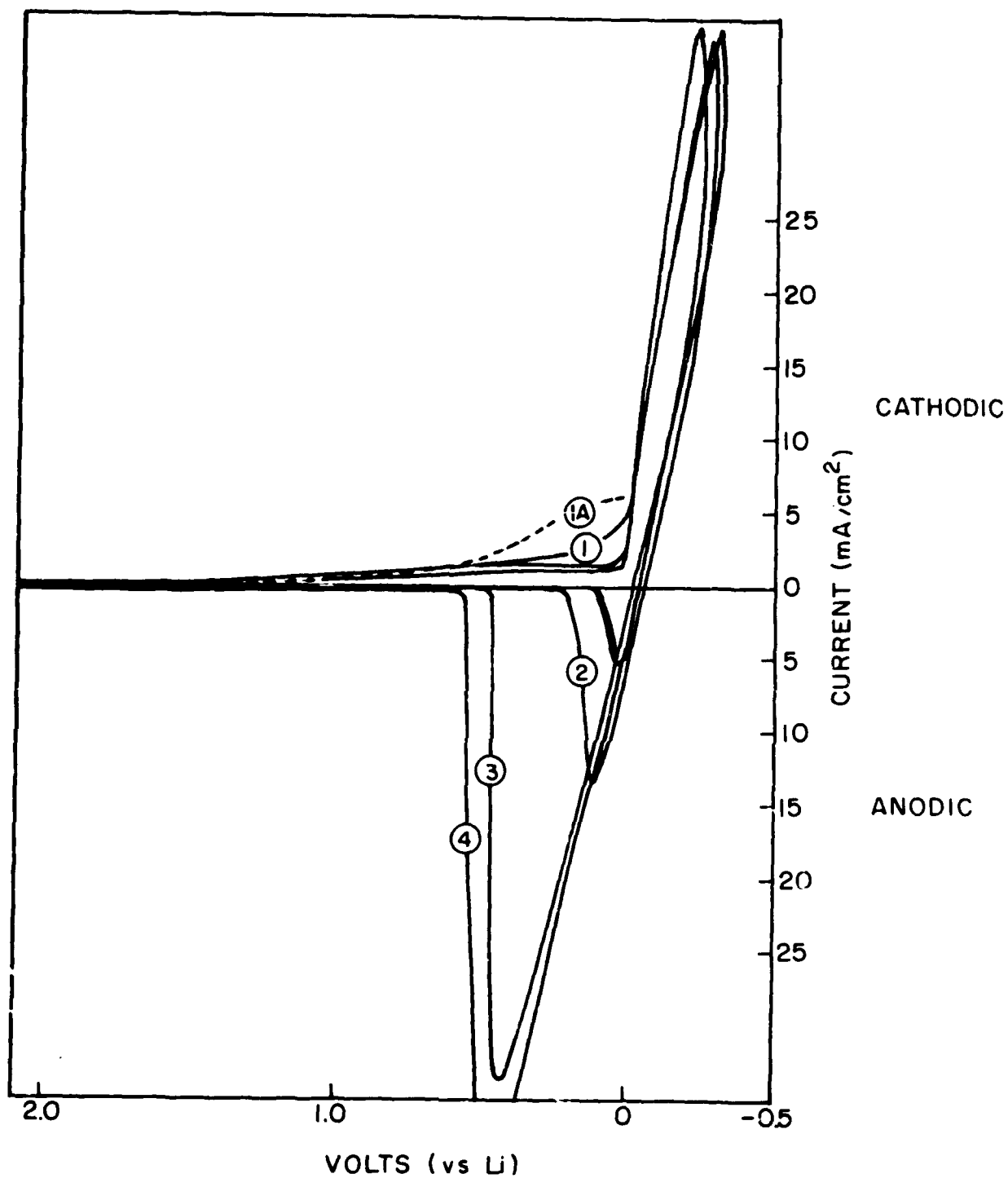
7

Fig. 4: Cyclic voltammogram of 1M LiClO₄ in methyl acetate on
nickel. Sweep speed = 0.1 V/sec. T = 25°C. (1) first
sweep; (1A) second sweep; (2) 200 ppm nitromethane added;
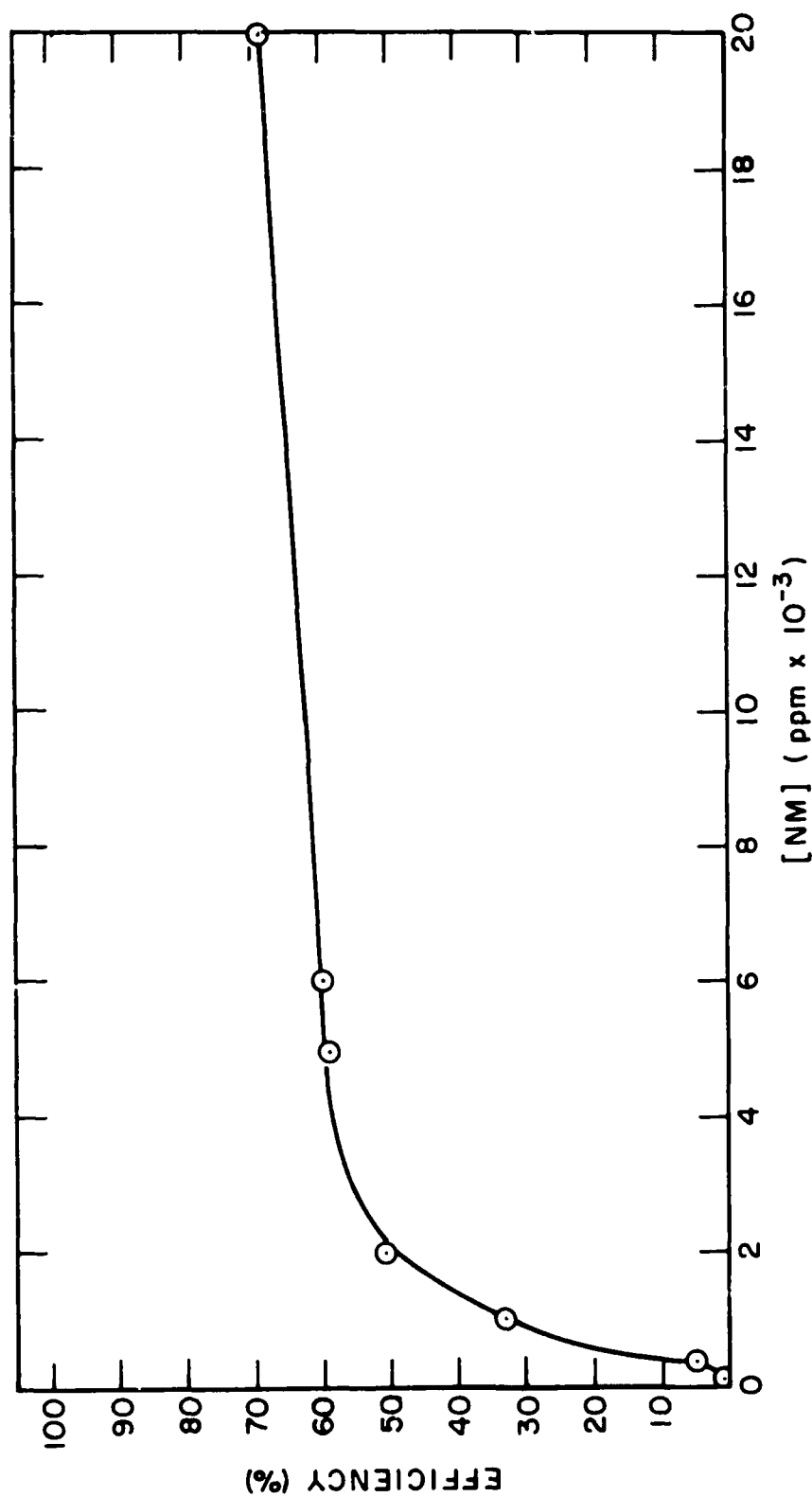(3) 1000 ppm nitromethane added; (4) 20,000 ppm nitro-
methane added.

8

Fig. 5: Effect of nitromethane concentration on the lithium cycling efficiency on a nickel substrate in methyl acetate, 1M LiClO4. Plating current (i_p) = stripping current (i_s) = 5 mA/cm^2; Q_{plated} = 1 coul/cm^2.
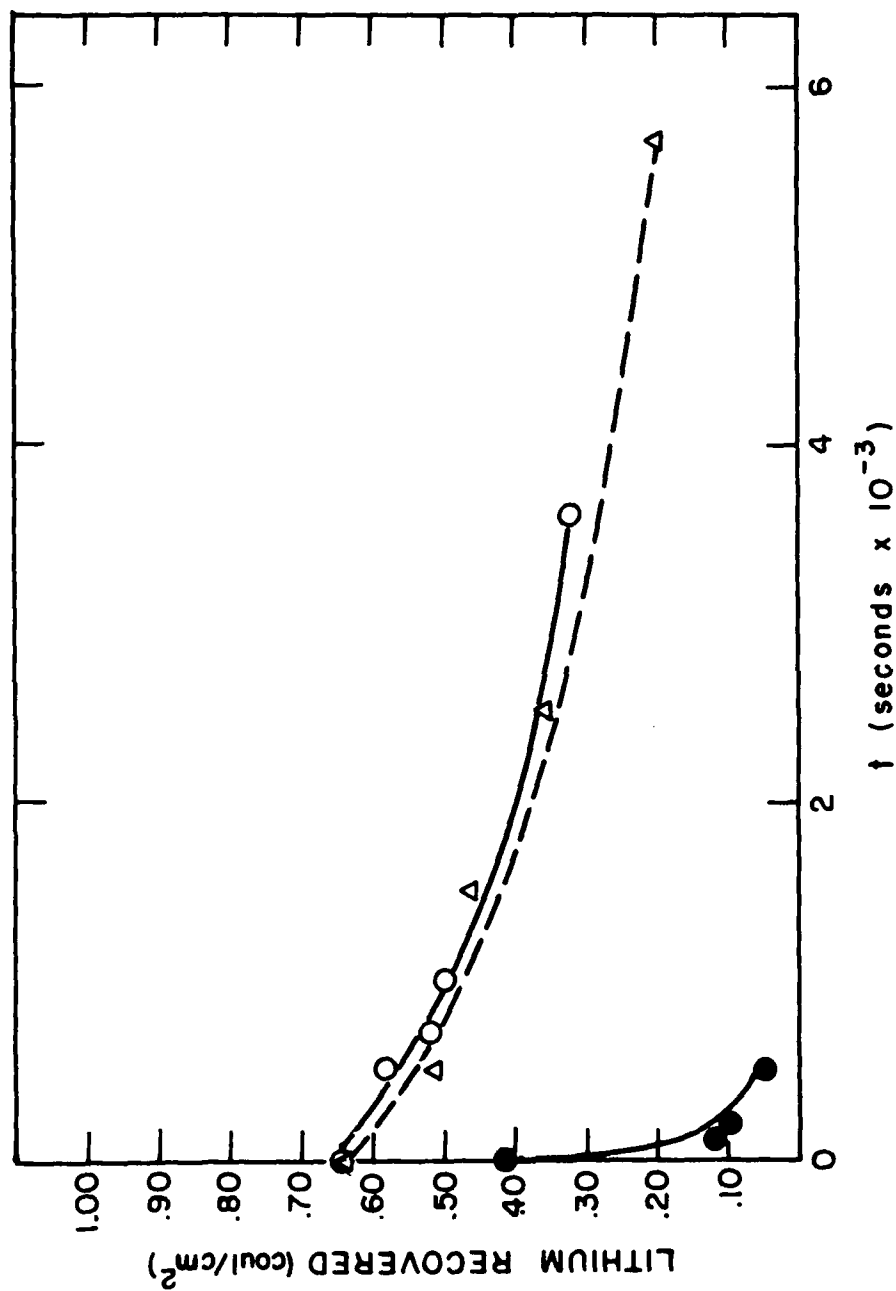
Fig. 6: Effect of nitromethane on the corrosion of lithium electrodeposited onto a nickel substrate in methyl acetate, 1M LiClO4. $i_p = i_s = 10$ mA/cm², $Q_p = 1$ coul/cm². (●) 2×10^3 ppm NM; (O) 10^4 ppm NM; (△) 10^5 ppm NM.
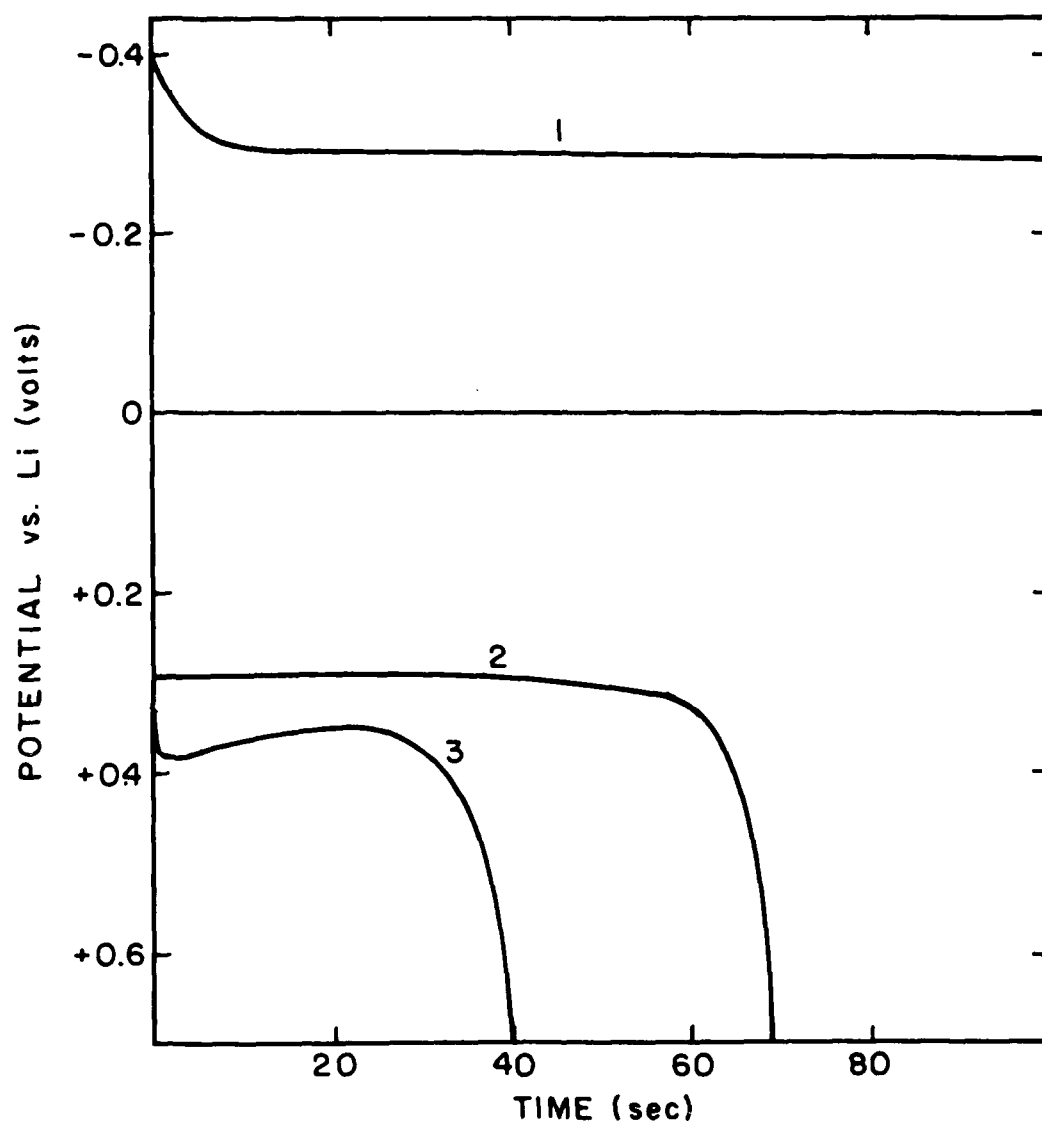
10

Fig. 7: Chronopotentiograms of lithium plating and stripping on a nickel substrate in methyl acetate, 1M LiClO4, 2% nitromethane. $i_p = i_s = 10$ mA/cm^2, $Q_p = 1$ coul/cm^2. (1) plating curve; (2) stripping curve after zero waiting time; (3) stripping curve after 4500 sec waiting time.

11

Fig. 8 presents the curve of efficiency as a function of cycle for a 2% NM solution in PC, 1M LiClO$_4$ (1 coul/cm^2, i_p = i_s = 10 mA/cm^2). The results show a slight improvement over those reported previously for PC, NM solutions (1), with the efficiency being maintained in excess of 60% for 50 cycles.

4. Effect of SO$_2$ on Lithium Cycling. The efficiency and cycling behavior of the MA, 1M LiClO$_4$, SO$_2$ system was examined. Fig. 3 shows that the efficiency of plating lithium in a 3M SO$_2$ solution is strongly dependent on i_p below 5 mA/cm^2. In a cell with a separator, the plateau of the efficiency curve corresponds to about 60%. In an open electrolyte cell, 70% efficiency is routinely observed under the same plating conditions (5-10 mA/cm^2).

For the first cycle (1 coul/cm^2, i_p = i_s = 10 mA/cm^2), a large jump in efficiency was noted for solutions containing greater than 0.01M SO$_2$. Below this concentration, efficiencies were below 20%, and somewhat irreproducible. Fig. 9 presents the efficiency of lithium cycling as a function of cycle number and SO$_2$ concentration. A solution 6 x 10^{-3}M in SO$_2$ shows behavior similar to the electrolyte without additives. The efficiency was 5% over five cycles. A 9 x 10^{-3}M SO$_2$ solution yielded a first-cycle efficiency of 20%, with successive cycles at the 5% level. Waiting between cycles produced no increase in efficiency for either electrolyte. Electrolytes containing higher concentrations of SO$_2$ showed initial efficiencies of 55 to 72%. The efficiency showed a general decline over the first five cycles, the magnitude of the decline being dependent upon (SO$_2$). Waiting 1000 seconds produced some recovery of efficiency ("spiking"), the magnitude of which was also directly proportional to (SO$_2$). Finally, the efficiency generally decreased more rapidly after each successive recovery, especially for the electrolytes of lower SO$_2$ concentration. "Spiking" was less pronounced and the efficiencies generally higher for the 3.0M SO$_2$ solution. Such behavior indicates the depletion of the local SO$_2$ concentration during the plating-stripping cycle, probably due to its reduction. As with PC, this "spiking" of the efficiency vs. cycle curves is much more obvious with added SO$_2$ than with NM.

As reported above, differences in cycling efficiency and corrosion rate were observed for cells with free electrolyte compared to cells with separators, at least in electrolyte containing 1200 ppm H$_2$O. The fiberglass separator only affected the corrosion rate in cells containing 3M SO$_2$. The separator apparently limits the diffusion of solution species to the electrodeposit during plating, thus limiting the positive effect of the additive on the cycling efficiency if it is present at low concentration. The better effect of SO$_2$ on i_c in the closed configuration may mean that the corroding solution species is being depleted in the vicinity of the electrode in presence of the separator. It could be, however, that the separator lowers the
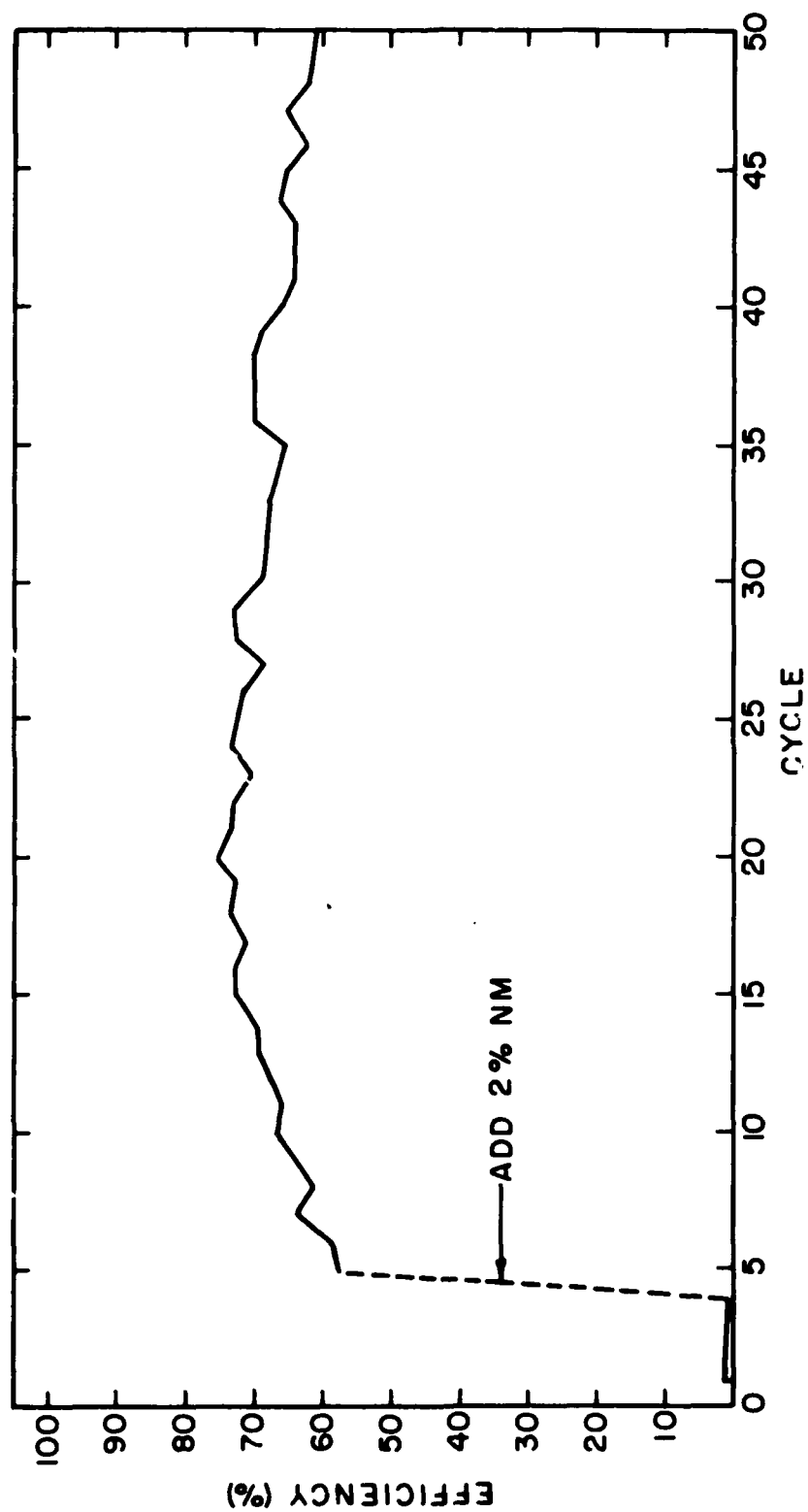
12

Fig. 8: Efficiency of cycling lithium on a nickel substrate in methyl acetate, 1M LiClO$_4$, 2% nitromethane (NM) as a function of cycle number. $i_p = i_s = 10$ mA/cm^2, $Q_p = 1$ coul/cm^2.
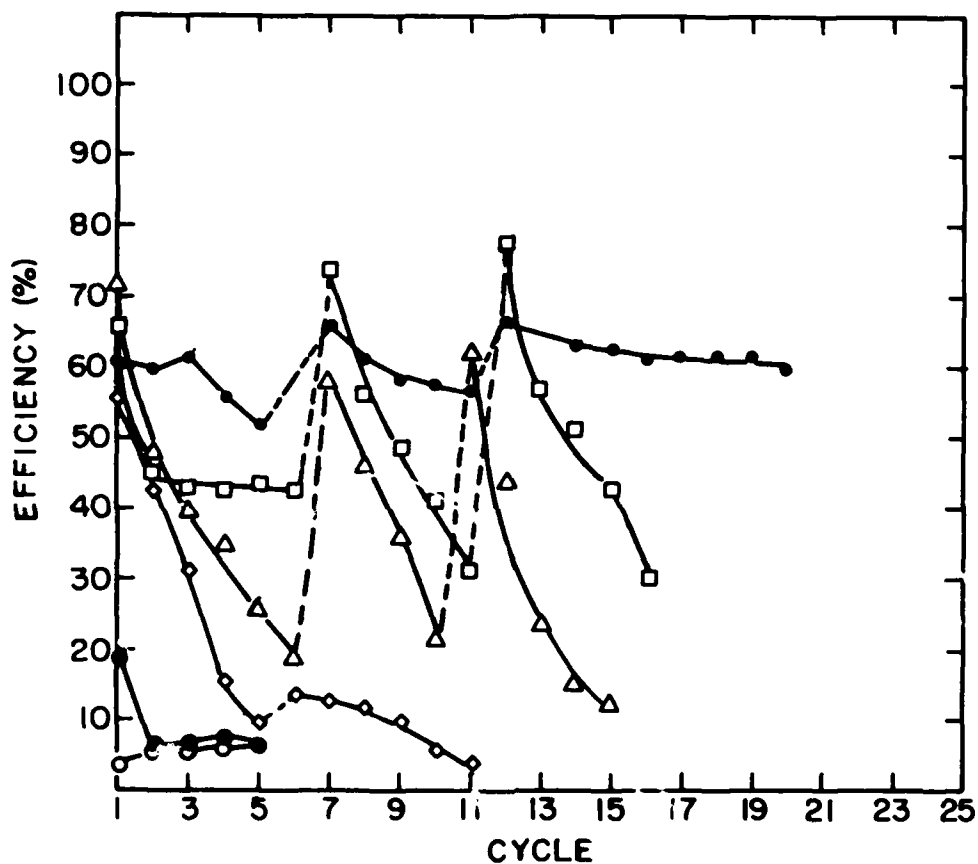
Fig. 9: Efficiency of cycling lithium on a nickel substrate in methyl acetate, 1M LiClO4 as a function of added SO2 concentration and cycle number. $i_p = i_s = 10$ mA/cm^2, $Q_p = 1$ coul/cm^2. (O) 6 mM SO2, (●) 9 mM SO2, (◉) 12 mM SO2, (Δ) 18 mM SO2, (▣) 30 mM SO2, (•) 3M SO2. (---) indicates a 1000 sec wait between cycles.

14

corrosion rate in the presence of additives because of morphological differences imposed upon the plated metal by the tightly closed configuration.

The corrosion rate of electrodeposited lithium was measured in MA/SO_2 solutions. A saturated solution contains about 3M SO_2, so this concentration was chosen for study. Corrosion was investigated in both closed (i.e., separator) and open (free) electrolyte cells. The results appear in Fig. 10. Corrosion in the open electrolyte cell shows considerable scatter. Nevertheless, a marked reduction in corrosion rate with time is evident for both cell configurations, reaching a limiting value of about 15 $\mu A/cm^2$ in the open electrolyte cell, and falling effectively to 0 $\mu A/cm^2$ in the closed electrolyte cell.

Chronopotentiograms, shown in Fig. 11, suggest the buildup of a film on the electrodeposited lithium during open circuit stand. As in the case of NM, a slight anodic overshoot is evident at the beginning of the stripping cycle, with the stripping potential remaining higher than for stripping without waiting. In the case of SO_2, the stripping potential shifts by as much as 120 mV. This indicates a more resistive film than with NM.

DISCUSSION

In a previous paper (1), a mechanism for the corrosion of electro- plated lithium in electrolytes based on PC was presented. Additives, it was suggested, form Li^+-conductive films on the metal during deposi- tion. These, to some degree, prevent the buildup of insulating films due to reaction of lithium with the solvent (solution). Cycling inefficiency was ascribed to the encapsulation of the deposit by such insulating products. This mechanism accounts for the observed increase in cycling efficiency in the presence of the additives. During open circuit stand, the partially soluble, Li additive, conductive films are gradually replaced by insoluble insulating films, e.g., from reac- tion with solvent, resulting in the loss of electrical contact of some granules of lithium from the substrate. Although little actual lithium is reacted chemically during this process (6), the rate of loss of electrical contact was found to be equivalent to 10-40 $\mu A/cm^2$ in PC.

MA corrodes electrodeposited lithium considerably faster than does PC. This may be due in part to greater solubility of the reaction products of MA and lithium, leading to a continually exposed metal surface. Such a high solubility of the lithium-solvent reaction product is also suggested by the larger number of cycles generally obtainable for MA than for PC-based systems; physical examination of the electrodes shows ultimate failure is due to product accumulation on them. This higher solubility of the lithium-MA film allows for the buildup of more extensive films through reaction of lithium with the additive.
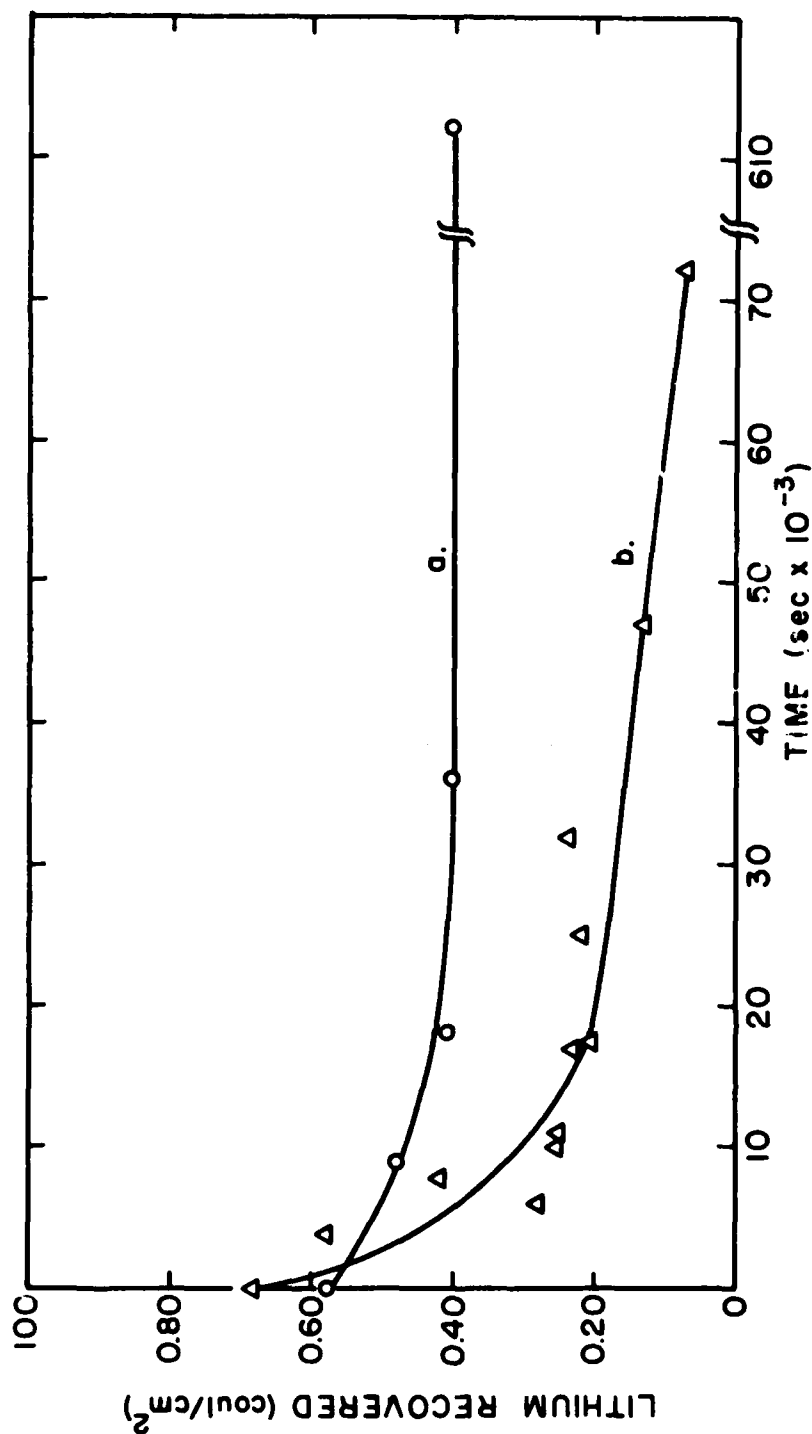
15

Fig. 10: Corrosion rate of lithium electrodeposited onto nickel in methyl acetate, 1M LiClO$_4$, 3M SO$_2$. $i_p = i_s = 5$ mA/cm^2, $Q_p = 1$ coul/cm^2. ($\triangle$) free electrolyte cell configuration, (O) tight cell configuration, with a fiberglass separator.
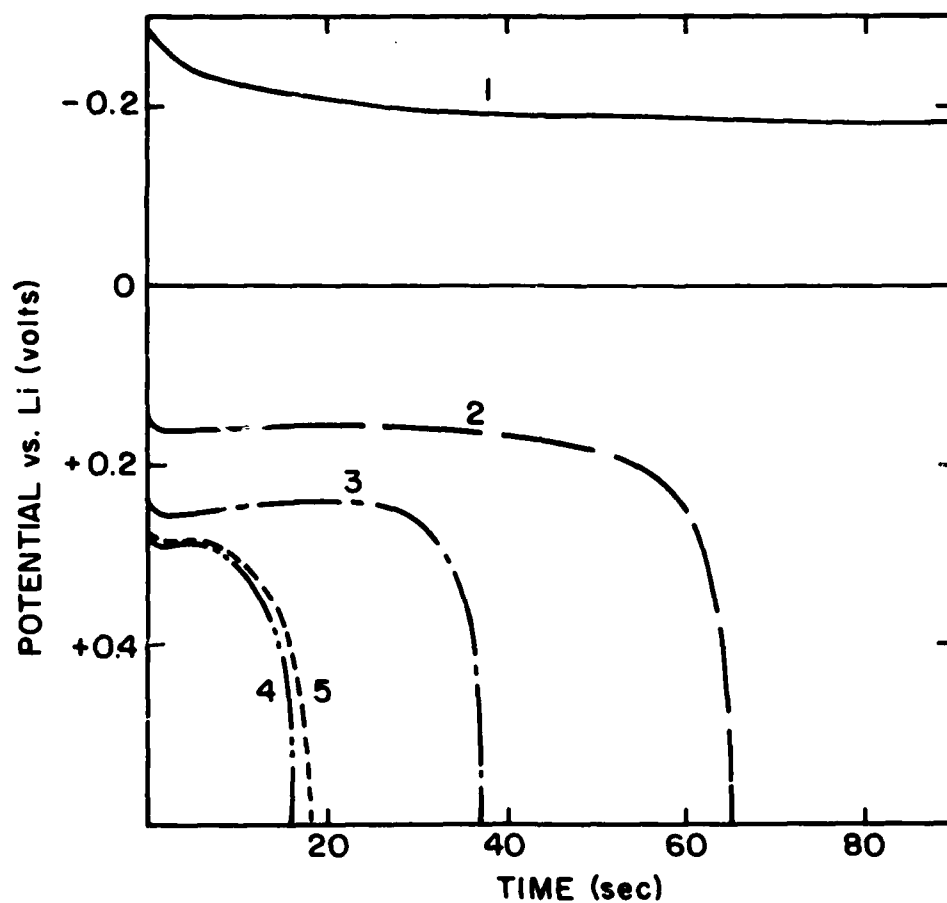
16

Fig. 11: Chronopotentiograms of lithium plating and stripping on a nickel substrate in methyl acetate, 1M $LiClO_4$, 3M SO_2. $i_p = i_s = 10$ mA/cm^2, $Q_p = 1$ coul/cm^2. (1) plating curve; (2) stripping curve after zero waiting time; (3) stripping curve after 750 sec waiting time; (4) stripping curve after 1750 sec waiting time; (5) stripping curve after 3200 sec waiting time.

17

Presumably due to the presence of such films, corrosion is retarded by added SO_2, NM and H_2O during open circuit stand as well as during plating.

A major point in this work with MA is that a unique combination of solvent and additive should be sought, such that (insulating) products formed by reaction of lithium and solvent are soluble, while products formed by reaction of lithium and additive are Li^+-conductive and insoluble. In this case, if reaction with the solvent is not too vigorous, passivation might be maintained during and after lithium deposition. The system which most closely fits this description is MA/SO_2, in which corrosion of electrodeposited lithium by the solvent could be prevented altogether.

REFERENCES

1. R. D. Rauh and S. B. Brummer, J. Electrochem. Soc. 0000 (1975). Technical Report No. 1 on this contract (Feb. 1975).

2. W. Meyers, Report No. 1, Contract NAS 3-6004 (Oct. 1964).

3. R. Jasinski, Adv. Electrochem. Electrochem. Eng., 8, 253 (1971).

4. R. Jasinski, Final Report, Contract NOW 64-0653-F (July 1965).

5. F. W. Dampier and P. E. Krouse, Abstracts of Fall Meeting of the Electrochemical Society, New York, New York (1974); Abstract No. 23.

6. R. Selim and P. Bro, J. Electrochem. Soc., 121, 1457 (1974).